PATENT SPECIFICATION

(11) 1 512 553

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(21) Application No. 40843/75 (22) Filed 6 Oct. 1975

(44) Complete Specification published 1 June 1978

(51) INT CL² A61L 15/07 C08F 2/50

(52) Index at acceptance

C3P KP

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(19)

(54) ORTHOPEDIC MATERIAL

(71) We, MITSUBISHI PETROCHEMICAL CO. LTD., a Japanese Body Corporate of 5—2, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement.—

This invention relates to a photocurable flexible orthopedic material such as a bandage or splint, and a method for producing it.

Orthopedic bandages composed of calcined gypsum and a fibrous base material such as gauze have been used from old to cover or fix members of a body, for example, in the treatment of bone fracture. These bandages, however, have the defect of heaxy weight, insufficient strength, poor water resistance and impermeability to X-rays.

United States Patent 3,089,486 discloses an improvement of such a bandage containing gypsum. This bandage, however, suffers from various disadvantages. For example, because of using a curable low-boiling methacrylate monomer, it gives off an unpleasant odor. It has poor storage stability, and therefore, must be used immediately upon impregnation. Also, the curing of the monomer is time-consuming.

In an attempt to make further improvement, therefore, photocurable orthopedic bandages using an ultraviolet curable polymer have recently been developed. United States Patent 3,421,501 suggests an orthopedic bandage produced by impregnating a glass fiber cloth or fabric with a photocurable unsaturated polyester. The unsaturated polyester, however, essentially requires the addition of a cross-linking monomer compatible with it, such as styrene, methyl styrene or methyl methacrylate. Since such a monomer to be added to the unsaturated polyester is mainly a low-boiling compound, it is very liable to evaporate before the completion of curing. Thus, when the bandage is used to dress wounds, it gives off a very unpleasant odor. Furthermore, styrene or the like monomer is known to have an irritating action, and exhibit a medium degree of toxicity (transitory irritation) toward skins, eyes and mucous membranes (N. Irving Sax, "Dangerous Properties of Industrial Materials", Vol. 2, page 1090, 1963). Because of such a toxicity, the volatilzation of a vapor of such a monomer is undesirable both to patients and persons who dress them with bandages. Moreover, since the volatilization of such a monomer causes a change in the composition of the bandage impregnated with the unsaturated polyester resin, the storage stability of the bandage after unsealing is poor, and when the bandage is stored for long periods of time after unsealing, it cannot retain sufficient strength.

Furthermore, since the unsaturated polyester resin itself which is suited for bandages has an extremely high viscosity, and is difficult to impregnate directly in a base material such as a fibrous material, it is necessary to dilute the polyester resin with a suitable solvent before impregnation, and after impregnation, remove the solvent. It is extremely difficult to remove only the solvent without removing the volatile monomer added to the unsaturated polyester. In this regard, too, the chemical composition of the resin is difficult to maintain constant. The United States Patent 3,421,501 also suggests the use of triallyl cyanurate, a high-boiling monomer, instead of the volatile monomer. But this monomer presents difficulties in actual application because it is irritating to the skin and has poor photocurability.

Because the unsaturated polyester of such a bandage is cured while the bandage is being applied to a member of a body, it cannot be cured by heating, but is cured substantially at room temperature. Thus, the odour of the monomer such as styrene does not disappear even after curing, and the patient is compelled to endure the bad

smell for long periods of time. This is inconvenient in actual application of such a bandage.

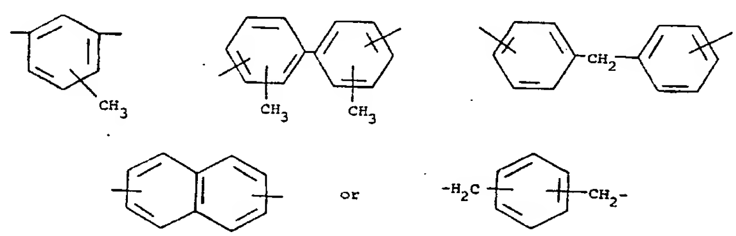
The present invention provides a photocurable flexible orthopedic material such as a bandage or splint which can be applied to members of a body and which is free from volatile monomer and solvent and has good storage stability.

The present invention thus provides a storage-stable flexible photocurable orthopedic material comprising a flexible fabric impregnated with a photosensitizer and a photocurable tacky composition in an amount from 25 to 50% by weight based on the combined weight of the fabric and the tacky composition, said tacky composition having been obtained by reacting (A) at least one hydroxyalkyl acrylate or methacrylate with the hydroxyalkyl portion containing 2 or 3 carbon atoms, with (B) 0.55 to 3 moles, per mole of the hydroxylalkyl acrylate or methacrylate (A), of at least one diisocyanate of the formula:

$$OCN—R_1—NCO$$

wherein R_1 represents

$$—(—CH_2—)_6—$$



to form a reaction product containing residual free isocyanate groups, and reacting said reaction product with from 1 to 2 equivalents, based on the residual free isocyanate groups in said reaction product, of (C) at least one polyhydric alcohol of the formula:

$$R_2(OH)_m$$

wherein R_2 represents a straight-chain or branched chain saturated aliphatic hydrocarbon group containing 2 to 8 carbon atoms, a cycloaliphatic hydrocarbon group, or the group

$$—CH_2\underset{R_3}{\underset{|}{C}}H(OCH_2\underset{R_3}{\underset{|}{C}}H—)_n—$$

in which *n* is an integer from 1 to 4 and R_3 is a hydrogen atom or a methyl group, and *m* is 2 or 3,

to form a tacky composition containing at least one compound containing at least two carbon-carbon double bonds capable of being polymerised and crosslinked by light and substantially free of compounds containing free isocyanate groups.

The characteristic feature of the orthopedic material of the invention is that the photocurable tacky composition used to impregnate the fabric is prepared from components (A), (B) and (C).

The tacky photocurable composition used in this invention differs from a known composition comprising a high viscosity unsaturated polyester and a low viscosity crosslinking agent such as styrene and capable of being crosslinked by irradiation of ultraviolet rays, and comprises compounds of a relatively low molecular weight. It cures as a result of the polymerization and crosslinking of at least two functional groups (i.e. (meth)acrylate groups) of at least one compound in the composition by irradiation of light in the presence of a photosensitizer. Accordingly, the tacky photocurable composition used in this invention does not require a volatile cross-linking agent (monomer) such as styrene, is odorless, and has a very fast rate of curing.

The polymer used in the conventional resin-impregnated bandages is highly viscous before impregnation and a volatile crosslinking monomer is required to dilute it. In contrast, in the orthopedic material of this invention, a specific photocurable composition of a relatively low molecular weight is used, and no volatile monomer is

required, and moreover, after using the composition to impregnate fabric, it can be cured by polymerization.

The tacky composition is prepared from components (A), (B) and (C) in the following manner.

First, from 0.55 mole to 3 moles of the diisocyanate (sometimes abbreviated to "D") is added to 1 mole of the hydroxyalkyl acrylate or methacrylate (sometimes abbreviated to "acrylate" or "H") to react the isocyanate groups of the diisocyanate with the hydroxyl group of the acrylate. This reaction affords a mixture of an adduct resulting from the addition of one molecule of the acrylate to one molecule of the isocyanate (sometimes abbreviated to "H . D adduct") and an adduct resulting from the addition of 2 molecules of the acrylate to one molecule of the diisocyanate (sometimes abbreviated to "H . D . H adduct"). After the completion of the reaction of the hydroxyl groups of the acrylate with the isocyanate groups of the diisocyanate, the polyhydric alcohol, i.e. a glycol or triol (sometimes abbreviated to "G"), is added in an amount such that the amount of hydroxyl groups provided is 100 to 200 equivalent %, preferably 105 to 150 equivalent %, of the isocyanate groups remaining in the H . D adduct and thereby to complete the reaction of the isocyanate groups of the H . D adduct with the hydroxyl groups of the polyhydric alcohol and to form a product resulting from the addition of one or more molecules of H . D to the polyhydric alcohol, for example, a mixture of the H . D . G adduct and H . D . G . H adduct.

In the tacky composition prepared from components (A), (B) and (C), the proportions of the H . D adduct, H . D . G adduct and H . D . G . D . H adduct can vary according to the proportions of the acrylate, diisocyanate and polyhydric alcohol used, and besides the above adducts, polyadducts such as $H.(D.G)_n.D.H$ adduct or $H.(D.G)_n$ adduct can also be produced. These polyadducts also polymerize upon irradiation with light. It is essential that the tacky composition prepared from components (A), (B) and (C) contains at least one compound having at least two (meth)-acrylate groups therein such as H . D . H or H . D . G . D . H. Since these compounds contain at least two (meth)acrylate groups as functional groups, they polymerize and crosslink upon irradiation with light in the presence of a photosensitizer.

In the present invention, the reaction is carried out in two stages as mentioned above. This is because if any of the acrylate remains unreacted with the diisocyanate, it gives off an unpleasant odor, and is likely to cause inflammation or blistering upon contact with the skin. Thus, it is necessary to react the acrylate completely with the diisocyanate.

In the second stage of the reaction, the polyhydric alcohol is added so that the amount of the hydroxyl groups is from 1 to 2 equivalents of the isocyanate groups remaining in the H . D adduct. This is because of the need to react the isocyanate groups substantially completely so that the tacky composition does not contain free isocyanate groups. If free isocyanate groups were to remain in the tacky composition, the properties of the composition would be likely to change with time as a result of water absorption. This can be avoided by providing the hydroxyl groups in slight excess.

Examples of the hydroxyalkyl(meth)acrylate used as component (A) in this invention are 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate. They can be used either alone or as mixtures of two or more. Of these, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, and mixtures of these are especially preferred.

Examples of the diisocyanate used as component (B) in the present invention include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, hexamethylene diisocyanate, diphenylmethane diisocyanate, naphthylene diisocyanate, tolidine diisocyanate, and xylylene diisocyanate. They can be used either alone or as mixtures of two or more. Of these, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, hexamethylene diisocyanate, and especially mixtures of these are preferred.

Examples of the polyhydric alcohol as component (C) include ethylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,2-butanediol, 1,6-hexanediol, glycerol, trimethylol propane, trimethylol ethane, and cyclohexane dimethanol. Of these, diethylene glycol is especially preferred. They can be used either alone or as mixtures of two or more.

The proportion of the diisocyanate (B) is 0.55 to 3 moles, preferably 0.7 to 2 moles, per mole of the hydroxyalkyl (meth)acrylate (A), and the proportion of the polyhydric alcohol is such that the proportion of the hydroxyl groups is 1.0 to 2.0 equivalents, preferably 1.05 to 1.5 equivalents, based on the amount of the residual free isocyanate groups in the reaction product of (A) and (B). When the proportion

of the diisocyanate is less than 0.55 moles, some of the hydroxyalkyl (meth)acrylate remains unreacted, and is likely to cause an offensive odor. When it is more than 3 moles, the composition after photocuring is so hard as to make it unsuitable for use in the present invention. When the proportion of the hydroxyl groups of the polyhydric alcohol is less than 1.0 equivalent of the remaining isocyanate groups, undesirable free isocyanate groups remain in the final resin composition. On the other hand, when the proportion of the hydroxyl groups of the polyhydric alcohol exceeds 2.0 equivalents of the remaining isocyanate groups, the content of photopolymerizable carbon-carbon double bonds decreases excessively and unreacted polyhydric alcohol remains in a large quantity. Neither of these results is desirable.

The diisocyanate and the polyhydric alcohol can be used in part in the form of a reaction product. Such a reaction product can be obtained easily in the market. For example, a solution of a reaction product of 1 mole of trimethylol propane and 3 moles of tolylene diisocyanate is available from Bayer AG under the trademark Desmodur L. It can also be synthesized *in situ*.

Various photosensitizers can be used in the present invention, and examples include benzoin, benzophenone, azobisisobutyronitrile, naphthalenesulfonamide, and benzoin methyl ether. The amount of the photosensitizer suitably is 0.002 to 5% by weight, preferably 0.5 to 3% by weight, based on the weight of the photocurable composition used.

The flexible fabric used in this invention may, for example, be woven or non-woven fabrics made of mineral fibers such as glass fibers, animal or plant fibers such as wool, cotton or flax, and synthetic fibers such as polyamides or polyesters. Of these, the use of a flexible base material composed of glass fibers is especially preferred.

The production of the storage-stable, flexible photocurable orthopedic material fabrics of this invention will be described below.

The orthopedic material of this invention can be produced mainly by either of the following two methods.

One method comprises impregnating the flexible fabric with a tacky composition comprising a reaction product of components (A), (B) and (C) during the preparation of this composition. Specifically, it comprises (1) reacting the (meth)acrylate with 0.55 to 3 moles, per mole of the (meth)acrylate, of diisocyanate to form a reaction product in which free isocyanate groups remain, (2) adding the polyhydric alcohol to the reaction product of the first step to form a reactive composition, (3) impregnating the flexible fabric with the resulting reactive composition in the absence of a solvent before the reaction between the hydroxyl groups of the polyhydric alcohol and the free isocyanate groups is complete, (4) adding the photosensitizer in any of steps (1) (2) and (3), and (5) completing the reaction between the hydroxyl groups and the free isocyanate groups.

According to this method, the reactive composition obtained through steps (1) and (2) is itself a low viscosity liquid having a viscosity of 5 to 30 poises, preferably 10 to 20 poises, suitable for impregnation in the fabric. After impregnation, the reaction between the hydroxyl groups and the free isocyanate groups is completed to convert the liquid reactive composition into a non-flowable and tacky composition convenient for handling the impregnated fabric, for example, for applying to a body member. No solvent is used in this method, and therefore, no step is required to remove the solvent. The orthopedic material in accordance with this invention can thus be produced very advantageously.

It is important in this method that the flexible fabric should be impregnated with the reactive composition prepared in steps (1) and (2) at an initial stage of the reaction of the isocyanate groups remaining in the reactive composition with the hydroxyl groups of the polyhydric alcohol, and after impregnation, the above reaction is completed to consume the free isocyanate groups substantially. The above reaction can be completed by allowing the fabric impregnated with the reactive composition to stand for several to several tens of days at a temperature ranging from room temperature to about 40°C. in a light-shielded sealed condition.

The flexible fabric can be impregnated with the reactive composition by dipping the fabric in a bath containing the reactive composition and the photosensitizer, pulling it up from the bath, and squeezing it by, for example, rolls. Alternatively, the reactive composition may be coated on the fabric.

When the impregnation of the fabric is carried out continuously, the reactive composition immediately after the addition of the polyhydric alcohol is fed into the bath intermittently or continuously during the impregnation of the fabric so that an increase in the viscosity of the reactive composition will not cause difficulties in the impregnation of the fabric.

The other method of producing the orthopedic material comprises impregnating the flexible fabric with the tacky composition obtained by complete reaction of the components (A), (B) and (C), in the presence of a solvent, and then volatilizing the solvent. Specifically, it involves (1) reacting the (meth)acrylate with 0.55 to 3 moles, per mole of the (meth)acrylate, of the diisocyanate to form a reaction product in which free isocyanate groups remain, (2) reacting the reaction product from step (1) with the polyhydric alcohol to form a composition containing substantially no free isocyanate groups, (3) impregnating the flexible fabric with a solution of the composition from step (2), (4) adding the photosensitizer and a solvent inert to isocyanate groups either in step (1) or (2), and (5) volatilizing the solvent from the impregnated fabric.

The solvent used in this method should be inert to isocyanate groups and should have the property of dissolving the above composition. Examples are dichloromethane, diethyl ether, acetone, chloroform, dioxane and ethyl acetate.

The amount of the solvent is preferably adjusted to a minimum amount which causes the dissolution of the composition and makes it easy to impregnate the flexible fabric. In step (1) and/or step (2), the reaction can be accelerated by adding a urethanisation catalyst (for example, dibutyltin laurate, stannous octoate, N-methyl morpholine, N,N-dimethyl cyclohexylamine or an organic acid salt of 1,8-diazobicyclo (5.4.0)undecene-7 in an amount of 0.0001 to 1 equivalent percent based on the isocyanate groups.

In the methods described above, the amount of the tacky composition impregnated in the fabric is 25 to 50%, preferably 30 to 45%, based on the total weight of the fabric and the composition.

The orthopedic material so obtained can be applied to members of a body in the same way as known impregnated bandages of the photocurable type containing an unsaturated polyester resin, and can then be photocured. Specifically, when the orthopedic material of this invention is applied to the site of a bone fracture, for example, and exposed to light from an ultraviolet lamp or sunlight lamp, it is easily cured. Suitable light sources are those which emit large quantities of ultraviolet light of long wavelength regions, for example 3500 to 3800 Å. Desirably, the amount of the photosensitizer is adjusted so that the composition can be cured completely by exposure for 3 to 10 minutes.

The orthopedic material in accordance with this invention can be used not only as bandages but also as splints.

The following Examples will help to illustrate the present invention.

In these Examples, all parts and percentages are by weight unless otherwise specified.

The various properties shown in the examples were measured by the following methods.

Thickness of the cured bandage

Measured by a slide caliper.

Weight proportion of the fabric

A sample is calcined in an electric oven at 480°C., and the weight residue (%) is determined.

Weight proportion of the cured composition

Parts by weight per 100 parts by weight of the bandage.

Flexural rigidity of the cured bandage

Measured in accordance with ASTM D-747 by bending a specimen 10° on an Olsen-type flextural tester.

Viscosity

Measured by "Emila" (registered Trade Mark) "Rotary Viscometer" (a product of Reciprotor A/S, Denmark).

Example 1

(Preparation of Tacky Composition for Impregnation)

Four tacky compositions, Acrylate Urethane A, Acrylate Urethane B, Acrylate Urethane C, and Acrylate Urethane D, were prepared in the following manner.

Acrylate Urethane A

A reactor equipped with a stirrer, a water bath for heating and cooling, a temperature controller and a reflux condenser was charged with 34.8 parts (2 moles) of tolylene diisocyanate (2,4-:2,6-=80:20) and 23.2 parts (2 moles) of 2-hydroxyethyl acrylate, and they were reacted for 3 hours at 30°C. Furthermore, 0.35 parts of dibutyltin laurate was added as a urethanization catalyst, and the reaction was performed for 1 hour at this temperature.

Then, 11.1 parts (1.05 moles) of diethylene glycol and 69.4 parts of dichloromethane were added to the reaction product, and the mixture was reacted for 6 hours at 45°C. Then, the reaction mixture was cooled down to 20°C., and 2.8 parts of benzophenone was added. The product was stored in a brown receptacle for use in impregnation. This composition was designated as Acrylate Urethane A.

Acrylate Urethane B

The same procedure as in the preparation of Acrylate Urethane A was repeated except that 26.0 parts (2 moles) of 2-hydroxyethyl methacrylate was used instead of the hydroxyethyl acrylate and the amounts of dichloromethane and benzophenone were changed to 72.2 parts and 2.9 parts, respectively. The resulting composition was designated as Acrylate Urethane B.

Acrylate Urethane C

The same procedure as in the preparation of Acrylate Urethane A was repeated except that 8.0 parts (1.05 moles) of 1,2-propylene glycol was used instead of the diethylene glycol, and the amounts of dichloromethane and benzophenone were changed to 66.3 parts and 2.7 parts respectively. The resulting composition was designated as Acrylate Urethane C.

Acrylate Urethane D

The same procedure as in the preparation of Acrylate Urethane A was repeated except that 11.6 parts (1 mole) of 2-hydroxyethylacrylate and 13.0 parts (1 mole) of 2-hydroxyethyl methacrylate were used instead of 23.2 parts of the hydroxyethyl acrylate and 70.8 parts of diethyl ether was used instead of the dichloromethane. The resulting composition was designated as Acrylate Urethane D.

The infrared absorption spectrum of each of these compositions contained no characteristic absorption band (2280 cm^{-1}(ascribable to isocyanate groups, and this led to the confirmation that these Acrylate Urethanes A to D do not contain free isocyanate groups.

Example 2

Acrylate Urethane A was used to impregnate a glass cloth tape (WF-300 5N, a product of Nitto Spinning Co., Ltd.) in a darkroom, and the impregnated tape was placed in a brown desiccator. The dichloromethane solvent was removed by reducing the pressure in the desiccator for 30 minutes using an aspirator. Then, the Acrylate Urethane A was cured by exposing the impregnated tape for 3 minutes using an ultraviolet irradiation device ("Plano PS Printer A3", a product of Fuji Photographic Film Co., Ltd.) to form a cured tape having high rigidity and the following properties.

Before curing, the impregnated tape (bandage) was soft and tacky, and even when it was allowed to stand indoors for more than 30 minutes, a weight loss upon drying was less than 0.5% and it was substantially odorless.

Thickness	0.368 mm
Weight proportion of the fabric	69%
Weight proportion of the cured composition	31%
Flexural rigidity	7100 Kg/cm²

Example 3 (Comparison)

The same glass tape as used in Example 2 was impregnated with Rigolac 150 HR (an alkyd-styrene unsaturated polyester resin of the isophthalic acid type with a styrene content of 30%, a product of Showa Kobunshi Kogyo Co., Ltd) and allowed to stand indoors at 25°C. After a lapse of 30 minutes, the weight loss was 8.5%, and 26% of the styrene contained was lost. At this time, an unpleasant odor of the styrene filled the room.

Example 4

The procedure of Example 2 was repeated except that a mesh leno-weave glass cloth tape (WG 310, a product of Nitto Spinning Co., Ltd., calcined for 8 hours at

450°C.) was used instead of the glass cloth tape in order to improve its air-permeability. A cured tape having the following properties was obtained.

Thickness	1.10 mm
Weight proportion of the fabric	62%
Weight proportion of the cured composition	38%
Flexural rigidity	1400 Kg/cm²

Example 5

The same procedure as in Example 2 was repeated except that a polypropylene woven cloth tape (Yuka Cross Sheet, a product of Mitsubishi Petrochemical Co., Ltd.) was used instead of the glass cloth tape. The resulting cured tape had the following properties.

Thickness	1.0 mm
Flexural rigidity	1600 Kg/cm²

Examples 6 to 9

A cylindrical structure made of paperboard with a diameter of 8 cm and a length of 30 cm was covered with a polyethylene film. A bandage with a width of 6 cm was prepared by impregnating the same mesh leno-weave glass cloth tape as used in Example 4 with each of the Acrylate Urethanes A to D and then drying it. The bandage was wrapped around the polyethylene film-covered cylindrical structure, and the entire surface of the wrapped bandage was exposed to light from a sunlight lamp placed about 20 cm from it for an average of 3 minutes to cure the tacky composition in the bandage. After removal of the cylinder, all of the cured bandages were light in weight and had high rigidity and toughness.

Example 10

23.2 Parts (2 moles of 2-hydroxyethyl acrylate and 34.8 parts (2 moles) of tolylene diisocyanate (2,4-:2,6-=80:20) were reacted for 8 hours at 40 to 50°C., and then cooled. Then, 11.1 parts (1.05 moles) of diethylene glycol and 2.7 parts of benzophenone were added (no solvent was added) to form a reactive composition. The reactive composition was immediately used to impregnate the same glass cloth tape as used in Example 4, and the impregnated cloth tape was placed in a black polyethylene bag and allowed to stand for 2 weeks at room temperature. A small amount of the tacky composition was plucked off from the surface of the resulting photo-curable bandage, and analyzed by infrared absorption spectroscopy. No free isocyanate groups were detected.

The photocurable bandage was cured in the same way as in Examples 6 to 9. Almost the same results as in Examples 6 to 9 were obtained.

Example 11

29.0 Parts (2.5 moles) of 2-hydroxyethyl acrylate, 34.8 parts (2 moles) of tolylene diisocyanate (2,4-:2,6-=80:20), and 2.2 parts of benzoin methyl ether were reacted for 5 hours at 45 to 50°C. in a light-shielded condition, and the product was allowed to stand at room temperature for 2 days in a sealed container in the absence of light. Then, 10.6 parts (1 mole) of diethylene glycol was added at room temperature, and the mixture was immediately used to impregnate a glass cloth tape (WF-300 5N, a product of Nitto Spinning Co., Ltd.) in a darkroom. The impregnated glass tape was placed in a brown glass bottle, and allowed to stand at room temperature for 1 week. It was ascertained that no free isocyanate groups were present. The impregnated tape was cured by exposure of ultraviolet rays for 4 minutes in the same way as in Example 2. The resulting cured tape had the following properties.

Thickness	0.43 mm
Weight proportion of the fabric	55%
Weight proportion of the cured composition	45%
Flexural rigidity	6400 Kg/cm²

Example 12

35.2 parts (2.5 moles) of 2-hydroxyethyl methacrylate, 34.8 parts (2 moles) of tolylene diisocyanate (2,4-:2,6-=80:20) and 2.4 parts of benzoin methyl ether were reacted at 70°C. for 4 hours, and allowed to stand for 2 days at room temperature in a sealed container in the absence of light to afford a white solid product. The product was melted by heating it to 70°C., and immediately then, 10.6 parts (1 mole) of

diethylene glycol was added to form a liquid reactive composition. It was used to impregnated a tape in the same way as in Example 11, and the impregnated tape was allowed to stand and then exposed as in Example 11 to form a cured tape having the following properties.

Thickness	0.35 mm
Weight proportion of the fabric	66%
Weight proportion of the cured composition	34%
Flexural rigidity	8800 Kg/cm^2

Example 13

The same procedure as in Example 11 was repeated except that the amounts of the 2-hydroxyethyl acrylate, benzoin methyl ether and diethylene glycol were changed to 23.2 parts (2 moles), 2.1 parts, and 12.3 parts (1.16 moles), respectively. The resulting cured tape had the following properties.

Thickness	0.36 mm
Weight proportion of the fabric	65%
Weight proportion of the cured composition	35%
Flexural rigidity	5100 Kg/cm^2

Example 14

A person was bandaged at his elbow using a speed bandage (TE 1802—2, a product of Tokyo Eizai Lab. Co., Ltd.), and the uncured bandage obtained in Example 4 was then wrapped over the speed bandage. The uncured bandage was cured by exposure to a sunlight lamp placed about 20 cm away from it. During this time, neither the bandaged person nor the person who applied the bandage detected any offensive smell. The cured bandage fixed the elbow firmly. Hence, it was confirmed that the bandage could be used with good results as an orthopedic bandage.

Example 15

11.6 Parts (1 mole) of 2-hydroxyethyl acrylate, 19.5 parts (1.5 moles) of 2-hydroxyethyl methacrylate, 26.1 parts (1.5 moles) of tolylene diisocyanate (2,4-:2,6-= 80:20) and 8.4 parts (0.5 mole) of hexamethylene diisocyanate were reacted for 4 hours at 70°C., and cooled. The conversion of the hydroxyalkyl acrylate at this time was found to be 99% as a result of the determination of the amount of residual isocyanate groups.

Then, 10.6 parts (1 mole) of diethylene glycol and 2.3 parts of benzoin methyl ether were added to the reaction product. The resulting composition had a viscosity of 6 poises. The composition was rapidly used to impregnate a leno-weave glass tape (5 mesh, 10 cm wide, 36 g per meter, a product of Arisawa Seisakusho Co., Ltd.). The resulting impregnated bandage was placed on a polyethylene film, wound up, and placed in a black polyethylene bag in the same way as in Example 10. It was stored in a darkroom. Two weeks later, the impregnated glass tape was taken out, and wrapped in three layers around a polyvinyl chloride resin pipe, 75 mm in diameter, covered with a polyethylene film. It was then cured by exposing it for 1 to 4 minutes using a cylindrical irradiation device in which twenty 20W fluorescent lamps for photochemistry were arranged so that the inside diameter of the cylinder became 40 cm.

The cured product was removed from the polyvinyl chloride resin pipe, and its weight was found to be 60 g. Then, its flattening compression strength (rate of distortion 10%) was measured using a tensile tester (Autograph LIS-500, a product of Shimazu Seisakusho Co., Ltd.). The results were as follows:

After exposure for 1 minute	26 Kg
After exposure for 2 minutes	31 Kg
After exposure for 3 minutes	38 Kg
After exposure for 4 minutes	41 Kg
After exposure for 4 minutes and then standing for 24 hours	43 Kg
After exposure for 4 minutes and then standing for 48 hours	45 Kg

After use, the cured bandage could be easily stripped off by pulling its end by hand.

When the photocurable bandage was used after storage in a black polyethylene film bag for 6 months its strength was almost the same as above.

Example 16 (comparison)

The same glass tape as used in Example 15 was impregnated with an unsaturated polyester resin containing 3 wt% of benzoin methylether curable in air (Rigolac 158 BQT, a product of Showa Kobunshi Kogyo Co., Ltd.) (the resin content in the impregnated tape being 40%). Immediately then, it was wound up on a polyvinyl chloride resin pipe, and cured by exposure. Its flattening compression strength was as follows:

After exposure for 2 minutes	1 Kg
After exposure for 4 minutes	10 Kg
After exposure for 8 minutes	23 Kg
After exposure for 16 minutes	35 Kg
After exposure for 32 minutes	45 Kg

When it was allowed to stand for 2 days after exposure for 32 minutes, the offensive smell of styrene did not go away.

After use, the cured bandage could not be stripped off by hand, but could be removed only by using a plaster saw.

Example 17 (comparison)

A bandage impregnated with calcined gypsum (PLAS RUN-Gyps. T-1083, a product of Tokyo Eizai Lab. Co., Ltd.), 10 cm wide, was wrapped in 10 layers, and dried for 2 days. Its weight was 120 g. It was found to have a flattening compression strength of 30 Kg by the same method as in Example 15.

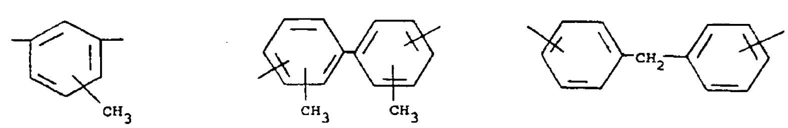
WHAT WE CLAIM IS:—

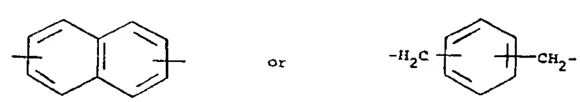
1. A storage-stable flexible photocurable orthopedic material comprising a flexible fabric impregnated with a photosensitizer and a photocurable tacky composition in an amount from 25 to 50% by weight based on the combined weight of the fabric and the tacky composition, said tacky composition having been obtained by reacting (A) at least one hydroxyalkyl acrylate or methacrylate with the hydroxyalkyl portion containing 2 or 3 carbon atoms, with (B) 0.55 to 3 moles, per mole of the hydroxyalkyl acrylate or methacrylate (A), of at least one diisocyanate of the formula:

$$OCN—R_1—NCO$$

wherein R_1 represents

$$—(—CH_2—)_6—$$





to form a reaction product containing residual free isocyanate groups, and reacting said reaction product with from 1 to 2 equivalents, based on the residual free isocyanate groups in said reaction product, of (C) at least one polyhydric alcohol of the formula:

$$R_2(OH)_m$$

wherein R_2 represents a straight-chain or branched chain saturated aliphatic hydrocarbon group containing 2 to 8 carbon atoms, a cycloaliphatic hydrocarbon group, or the group

$$—CH_2\underset{R_3}{CH}(OCH_2\underset{R_3}{CH}—)_n—$$

in which n is an integer from 1 to 4 and R_3 is a hydrogen atom or a methyl group, and m is 2 or 3,

to form a tacky composition containging at least one compound containing two carbon-carbon double bonds capable of being polymerised and crosslinked by light and substantially free of compounds containing free isocyanate groups.

2. An orthopedic material according to claim 1 wherein component (A) is selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate.

3. An orthopedic material according to claim 1 or 2 wherein component (B) is selected from 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and hexamethylene diisocyanate.

4. An orthopedic material according to claim 1, 2 or 3 wherein component (C) is selected from diethylene glycol, dipropylene glycol, tetraethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol and glycerol.

5. An orthopedic material according to any one of claims 1 to 4 wherein from 1.05 to 1.5 equivalents of component (C) were used to react with the reaction product of components (A) and (B).

6. An orthopedic material according to claim 1 substantially as described in any one of Examples 2 and 4 to 15.

7. A method of producing an orthopedic material as claimed in any one of the preceding claims, said method comprising the steps of:

(1) reacting the hydroxyalkyl acrylate or methacrylate (A) with 0.55 to 3 moles, per mole of the hydroxyalkyl acrylate or methacrylate (A), of the diisocyanate (B) to form the reaction product containing residual free isocyanate groups;

(2) adding the polyhydric alcohol (C) in an amount providing 1 to 2 equivalents of hydroxyl groups based on the amount of residual free isocyanate groups in said reaction product to provide a reactive composition;

(3) impregnating the flexible fabric with the reactive composition in the absence of a solvent before the reaction between the hydroxyl groups and the residual free isocyanate groups is complete and while the composition has a viscosity of 5 to 30 poises;

(4) adding the photosensitizer in any of steps (1), (2) and (3); and

(5) completing the reaction between the hydroxyl groups and the free isocyanate groups.

8. A method according to claim 7 wherein the polyhydric alcohol (C) is used in an amount providing 1.05 to 1.5 equivalents of hydroxyl groups based on the amount of residual free isocyanate groups in the reaction product of (A) and (B).

9. A method according to claim 7 substantially as described in any one of Examples 10 to 13 and 15.

10. A method of producing an orthopedic material as claimed in any one of claims 1 to 6, said method comprising the steps of:

(1) reacting the hydroxyalkyl acrylate or methacrylate (A) with 0.55 to 3 moles, per mole of the hydroxyalkyl acrylate or methacrylate (A), of the diisocyanate (B) to form the reaction product containing residual free isocyanate groups;

(2) adding the polyhydric alcohol (C) in an amount providing 1 to 2 equivalents of hydroxyl groups based on the amount of residual free isocyanate groups in said reaction product to form a composition containing substantially no free isocyanate groups;

(3) impregnating the flexible fabric with a solution of the composition from step (2);

(4) adding the photosensitizer and a solvent inert to isocyanate groups in the step (1) or (2); and

(5) volatilizing the solvent from the impregnated flexible fabric.

11. A method according to claim 10 wherein the reaction in step (1) and/or step (2) is carried out in the presence of a urethanization catalyst.

12. A method according to claim 10 or 11 wherein the polyhydric alcohol (C) is used in an amount providing 1.05 to 1.5 equivalents of hydroxyl groups based on the amount of residual free isocyanate groups in the reaction product of (A) and (B).

13. A method according to claim 10 substantially as described with reference to Example 1 in conjunction with any one of Examples 2 and 4 to 9.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.